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SURFACTANT-ENHANCED IN SITU SOILS WASHING

J. NASH, R.P. TRAVER, D.C. DOWNEY

USEPA/HWERL WOODBRIDGE AVE EDISON NJ 08837-3679

SEPTEMBER 1987

FINAL REPORT

MARCH 1985 - APRIL 1986



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ENGINEERING & SERVICES LABORATORY AIR FORCE ENGINEERING & SERVICES CENTER TYNDALL AIR FORCE BASE, FLORIDA 32403

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PREFACE

This report was prepared by the Air Force Engineering and Services Laboratory, Air Force Engineering and Services Center (HQ AFESC/RDVW), Tynda!1 Air Force Base, Florida 32403, and the Environmental Protection Agency's Hazardous Waste Environmental Research Laboratory (EPA/HWERL), Edison, New Jersey 08837-3679, under Interagency Agreement 57931283-01-0.

This report summarizes laboratory and pilot-scale testing conducted between March of 1985 and April of 1986. The HQ AFESC/RDVW program manager was Douglas C. Downey, and the EPA/HWERL manager was Richard P. Traver.

This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NIIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

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SECTION I

INTRODUCTION

A. OBJECTIVE

The primary objective of this joint Air Force and Environmental Protection Agency (EPA) project was to demonstrate the feasibility of <u>in situ</u> soils washing using surfactant solutions. A secondary objective was to provide information to help develop a comprehensive strategy for the decontamination of fire training areas at all Air Force and Department of Defense (DOD) installations.

B. BACKGROUND

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1. General

Through the Installation Restoration Program (IRP), the Air Force has identified over 1300 chemically contaminated sites on nearly 200 installations across the United States. Many of these sites contain soils contaminated by organic or inorganic chemicals at shallow depths which create a long-term leaching threat to ground and surface waters.

Several methods of decontamination are under investigation by the Environics Division of the Air Force Engineering and Services Laboratory. These methods include soil incineration, chemical oxidation/dechlorination and biological treatment. In recent years, the EPA has developed an <u>in situ</u> soils washing process through the Chemical Countermeasures Program managed by the Hazardous Waste and Engineering Research Laboratory, Releases Control Branch, Edison, New Jersey. Numerous laboratory studies have been completed showing 80 percent removal of crude oils and PCBs from soil columns washed with surfactant solutions.*

2. Site Selection Criteria

The following criteria were used in identifying the site most suitable for a soils-washing field demonstration. A site of less than 1 acre was desired to reduce soil variability and reduce sampling costs. Because soil washing is best suited for permeable soils, a sandy site was desirable.

^{*}Ellis, W.D., Payne, J.R., "Treatment of Contaminated Soils with Aqueous Surfactants," Interim Report to EPA Releases Control Branch, 6 Sep 85.

Contaminants at the site were to be common organic chemicals found at many other Air Force sites. Officials of the selected installation and responsible environmental agencies would have to cooperate to minimize permitting and approval time.

3. Review of Air Force IRF Reports

Preliminary screening of candidate sites was accomplished through a review of Air Force IRP reports (Reference 1). Over 60 reports and nearly 800 sites were screened. It became apparent that most sites with organic chemical contamination fell into two common categories: fuel spills and fire-training areas. Fire-training areas were especially suited to this research because of their limited size and the wide range of contaminants, which included both chlorinated solvents and fuel components. Fire-training areas are found at almost all Air Force installations. Long-term fuel and solvent dumping at these sites has created a significant pollution potential.

4. Selection of Volk Field Fire-Training Area

Following this careful review, a fire-training area at Volk Field Air National Guard (ANG) Base WI was selected as a research site. Volk Field is an active ANG Base (also known as the 8704th Field Training Site) and is under the operational control at the Wisconsin ANG which uses the base to conduct realistic combat training. During the summer months, the base provides basic facilities for several summer encampments of up to 800 ANG personnel (see Figure 1).

Historical data indicates that the fire-training area (see Figure 2) may have been established as early as 1955 and has routinely received waste solvents, as well as contaminated and clean JP-4 fuel. The total liquid waste deposited at the site could be as much as 260,000 gallons (988,000 liters) over its 30 year history. An estimated 80 percent of these wastes were burned in fire-training exercises, leaving approximately 50,000 gallons (190,000 liters) to soak into the soil (Reference 1).

Because of concerns over the pollution potential of this site, ANG engineers conducted an exploratory site survey and sampling project in 1981. Twelve shallow well samples were analyzed for purgeable organics using EPA Methods 601 and 602. Table 1 summarizes 1981 findings which confirmed that both chlorinated solvents, fuels and oils had entered the shallow groundwater and that soils beneath the site were likely to contain similar contamination.

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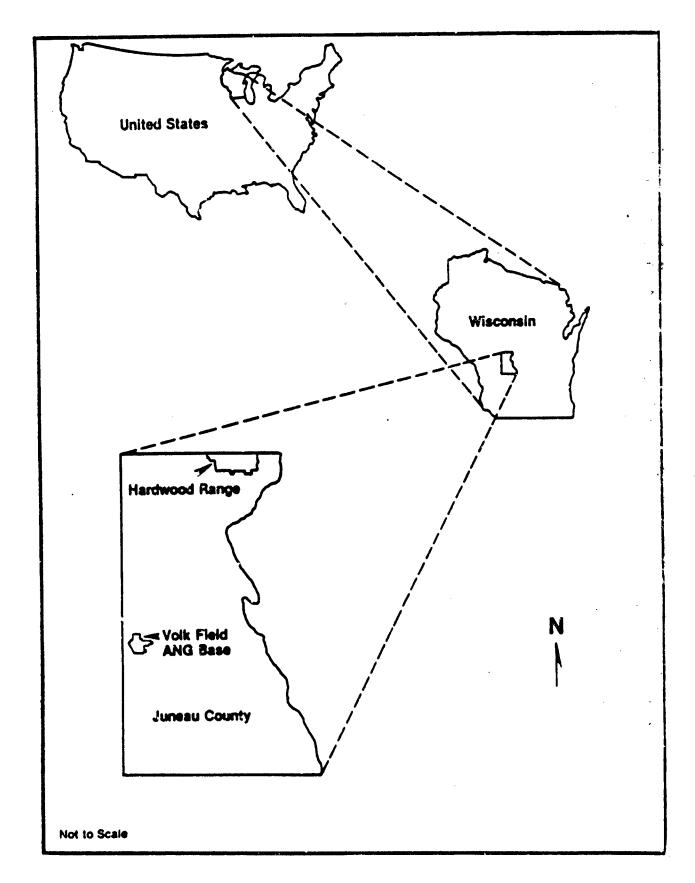


Figure 1. Location of Volk Field.

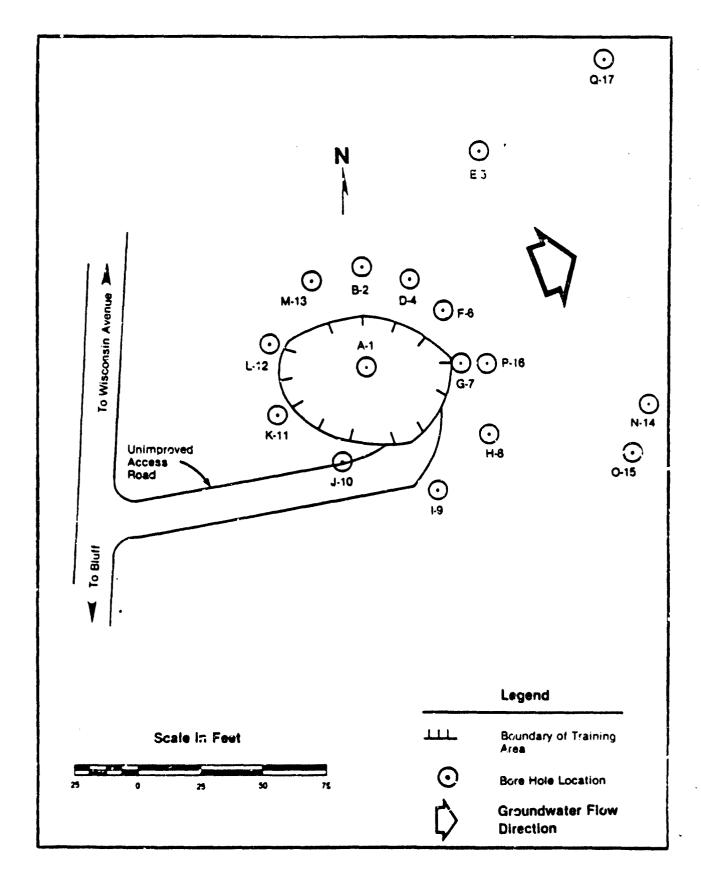


Figure 2. Site Map of Fire Training Area

TABLE 1. CHEMICALS FOUND IN SHALLOW WELLS VOLK FIELD 1981

I.G. Number		EPA Method 601 (ug/1)			EPA Method 602 (ug/l)	
	Chloroform	TCAª	TCE ⁵	Benzene	Toluene	Ethyl Benzene
A-1	2.3	<1.0	<1.0	4500.0	2700.0	270.0
B-2	2.3	<1.0	<1.0	<10.0	100.0	<10.0
0-4	1.5	7.8	22.0	570.0	2100.0	190.0
F-6	1.1	39.0	100.0	14000.0	8000.0	950.0
6-7	59.0	36.0	42.0	31000.0	36000.0	6800.0
H-8	130.0	<1.0	<1.0	1900.0	5700.ù	200.0
J-10	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
K-11	1.3	<1.0	<7.0	<7.0	4.6	<1.0
L-12	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
N-14	50.0	<1.0	<1.0	8.5	<1.0	2.9
0-15	1.0	<1.0	<1.0	<1.0	<1.0	<1.0
P-16	120.0	<10.0	<10.0	4000.0	50.0	1000.0

- a. 1,1,1 Trich!oroethane
- b. Trichloroethylene

In October 1984, the ANG Bureau in Washington, DC and the Base Civil Engineer at Volk Field were contacted concerning the possible use of the site. Their enthusiastic response led to a November 1984 meeting with the Wisconsin Department of Ratural Resources (WDNR) in which WDNR also indicate strong support for the research project. In May 1985, the WDNR received a more in-depth project briefing and continued to show their cooperation and full support for the project. With this assurance, a detailed site investigation was initiated in early June.

SECTION II

SITE CHARACTERIZATION

Four months before the field project, a complete site characterization was made to determine the extent and type of contamination at the fire training pit. Characterization included: the drilling and sampling of shallow bore holes, the installation of seven monitoring wells to depths of 40 feet (12.2 meters), the determination of the water table height and gradient, the determination of permeability, and the sampling and analysis of soil and water samples for volatiles and total organic carbon. From this study a greater understanding of the site and the contaminants was obtained (see Figure 3).

A. SOIL CHARACTERISTICS

The soil beneath the fire-training pit has been contaminated with waste oils, JP-4 jet fuel, and solvents used in maintenance functions around the base. The effect of such contamination on the soil is obvious when compared to nearby clean soil. The most obvious differences are color and lack of vegetation. The surface and near surface of the pit is black, cohesive, and free of any grass except at the edges of the pit (Reference 1). The pit emits an odor of fuel oil and the soil has enough residual contamination to feel oily. The natural soils near the pit have a thin organic layer that supports a grass cover. It is sandy, noncohesive, and light brown in color below the organic layer.

The grain size distribution of the soil under the pit is 95 percent sand with 5 percent by weight finer than sand. Soils outside of the pit are also sandy, but with 10 to 15 percent finer particles. The particle size distribution of the soil was determined by sieve analysis and is presented in figure 4. Additional sampling and sieve testing confirmed that the soil is a well-defined sand with a narrow particle size range. The sand is unconsolidated to a depth of 10 to 15 feet (3-4.5 meters), where a highly compacted sand is ancountered. This compacted material is described as weathered sandstone and may have some degree of consolidation although no evidence of consolidation was seen in disturbed split samples. Orillers measured standard penatration from N=8 near the surface to N=100 at 14 feet below ground level (BGL).

Mineralogically, both soils are at least 98 percent alpha quartz and have no clay, as determined by X-ray diffraction. The top of the fire pit has been

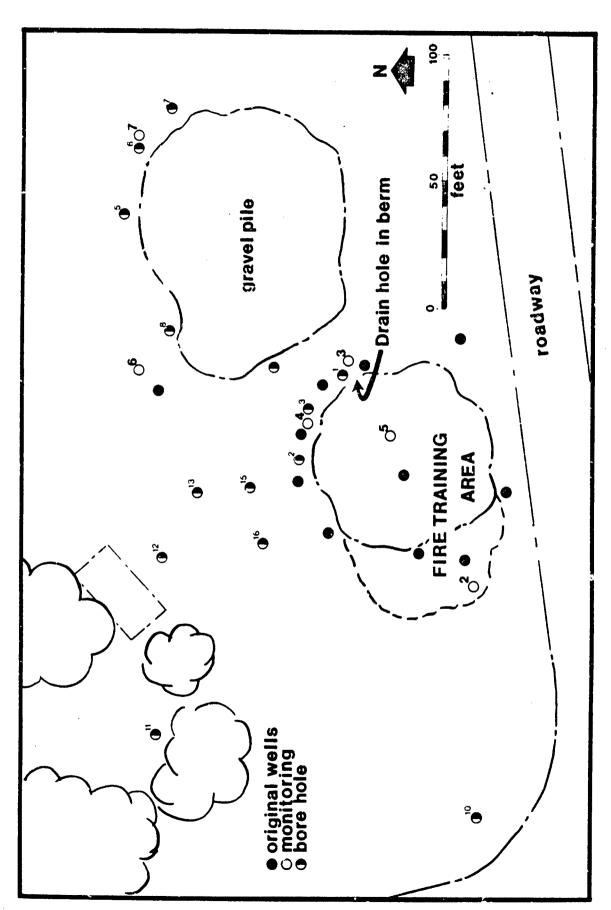


Figure 3. Spring 1985 Site Study

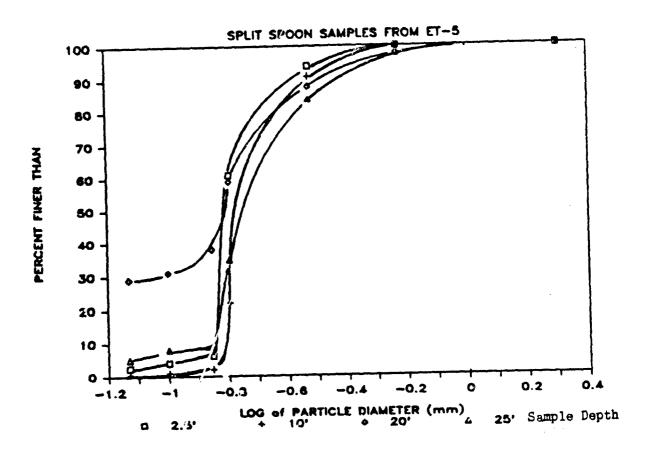


Figure 4. Soil Particle Size Distribution by Sieve Analysis

covered with a 4-inch layer of 60/40 gravel/sand. Underlying oil and vapors have infiltrated upward, contaminating this cover.

B. HYDROLOGIC PROPERTIES

The soil type at Volk Field is described as Boone fine sand. According to the Soil Conservation Service Engineering Field Manual, this is in hydrologic Soil Group A. Group A has high infiltration rates and low runoff potential. Standing water was observed after a rainfall, indicating that the fire pit has a low infiltration rate caused by surface oils. Runoff through a break in the berm has spread some contaminants to surface soil next to the pit.

The vertical permeability of the soil in the unsaturated zone was measured in a laboratory permeameter at 4×10^{-3} to 5×10^{-4} cm/sec. The permeability within the shallow aquifer was estimated by pump tests to be 5×10^{-2} cm/sec. According to measurements of water table elevations made at the site, groundwater flow increases in speed as it passes under the pit, perhaps due to some channeling in the fractured sandstone. The water table is in a highly weathered sandstone, and the aquifer extends to a depth of 700 feet (213 meters) without significant horizontal layering.

The mobilized contamination leaves the site via the groundwater initially in an easterly direction, and then turns to the northeast. The volume of soil and groundwater directly involved in this study was approximately 4,000 cubic yards (3,200 cubic meters) beneath the fire-training pit. Although the purpose of this study was not to define the outer limits of piume migration, indirect measurements using an electromagnetic (EM) survey technique indicated that the groundwater contamination may extend downgradient 250 feet (76 meters).

C. CHEMICALS AT THE SITE

Much of the contamination on the fire pit surface soils is waste crankcase oil. Comparatively smaller quantities of volatile organics and fuel-related hydrocarbons are present. Early in the project, the contamination of the aquifer was thought to be more confined in a floating fuel layer. This was not the case. Contaminants in the aquifer are emulsified hydrocarbons that have penetrated the aquifer at least 30 feet (9 meters).

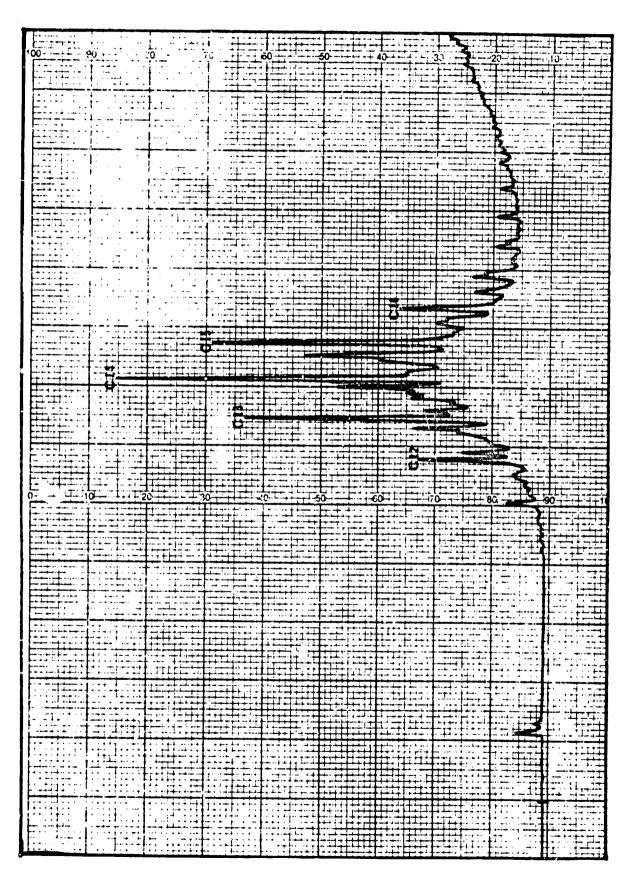
The nonvolatile chemicals, principally C-12 to C-16 hydrocarbons, comprise most of the contamination in the unsaturated zone ranging from 5,000 to 15,000 mg/kg (see Figure 5). An oil and grease analysis was used as the primary

indicator of soil contamination and was analyzed using a carbon tetrachloride (CCl₄) extraction. Long-term weathering had oxidized much of the oil and grease. These oxidized forms are more water-soluble than the nonoxidizel forms and were found in higher concentrations in the groundwater. Figure 6 shows the relationship between oil and grease and depth. Before installing monitoring wells, bore holes were made in and around the fire pit. Water samples taken from each bore hole at the water table were analyzed for total organic carbon (TOC). Figure 7 plots the TOC plume at the top of the water table. Total organic carbon (TOC) was used as the primary indicator of contamination in groundwater. Total organic carbon measurements as high as 760 mg/L were recorded in the most contaminated area of the plume. The deepest well drilled, ET-6, was 40 feet (12 meters) deep and traces (<10ppb) of benzene and toluene were found at the 40 foot level.

A limited number of gas chromatography (GC) analysis were performed to account for low molecular weight, more volatile compounds. Volatile organic compounds were low in concentration at the pit surface largely caused by volatilization to the atmosphere. As depth increased, measured levels of volatiles increased. Volatile chlorinated solvents or by-products detected in the soil and groundwater were 1,1,1 trichloroethane and trichloroethylene.

Nonchlorinated volatile compounds in the soil and groundwater include jet fuel components: benzene, toluene, xylene, and ethylbenzene. During the installation of monitoring wells, the driller's log was supplemented with gas chromatography (GC) measurements of the "headspace" above the soil samples. The soil's total volatile organic content at various depths was estimated using total GC counts. Figure 8 shows four volatiles versus depth logs. The first log is from upgradient Well ET-2. The remainder of the logs are from contaminated Wells ET-5, ET-3, and ET-4. Note that the "Counts" scale is a log scale.

The extremely high organic loading in the groundwater has depleted the oxygen within the local aquifer. This anaerobic or reducing condition has caused a significant increase in the soluble iron levels. The pH of the well field is 5.5 to 6.0. Atomic absorbtion analysis indicated dissolved iron levels as high as 24 mg/L in areas of high organic contamination. This iron precipitates in an organic-iron complex when exposed to air.



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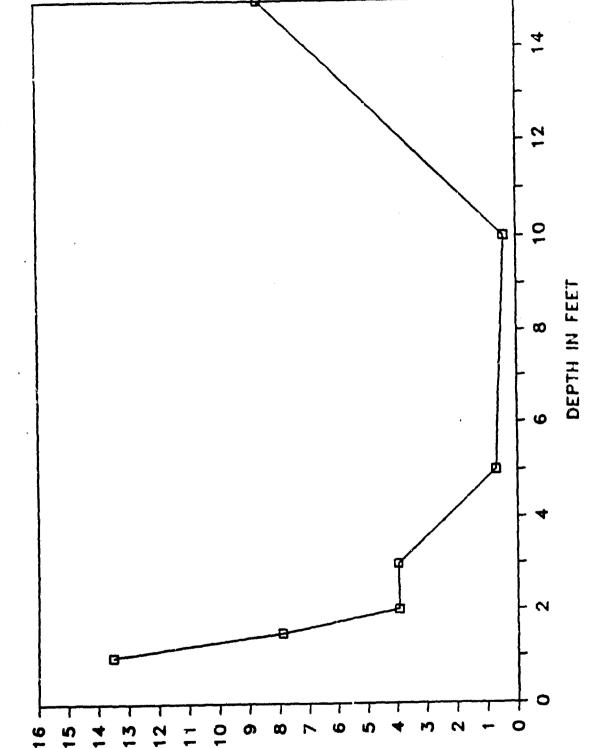


Figure 6. Oil and Grease Values as a Function of Depth

(Thousands)
OIF & GREASE (mg/kg)

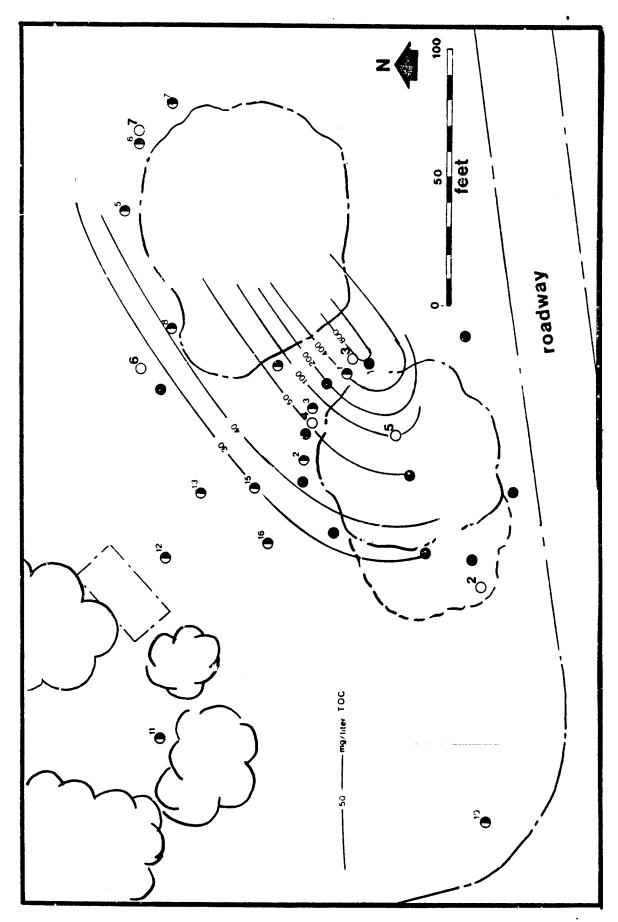
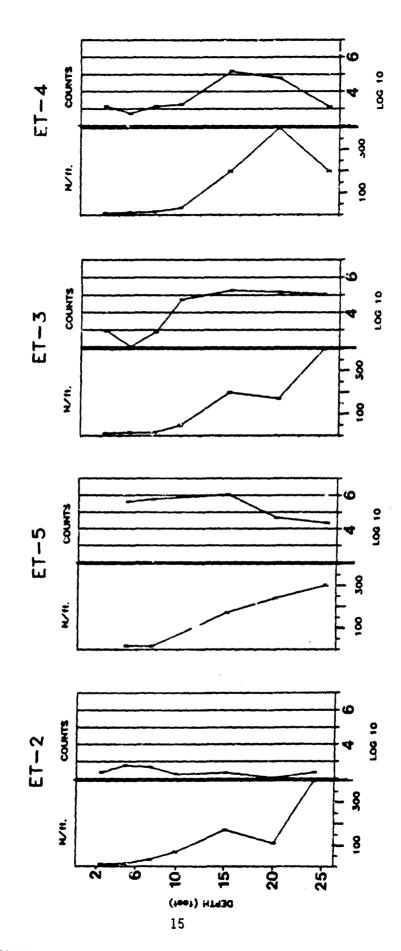


Figure 7. TOC Measurements of Shallow Groundwater



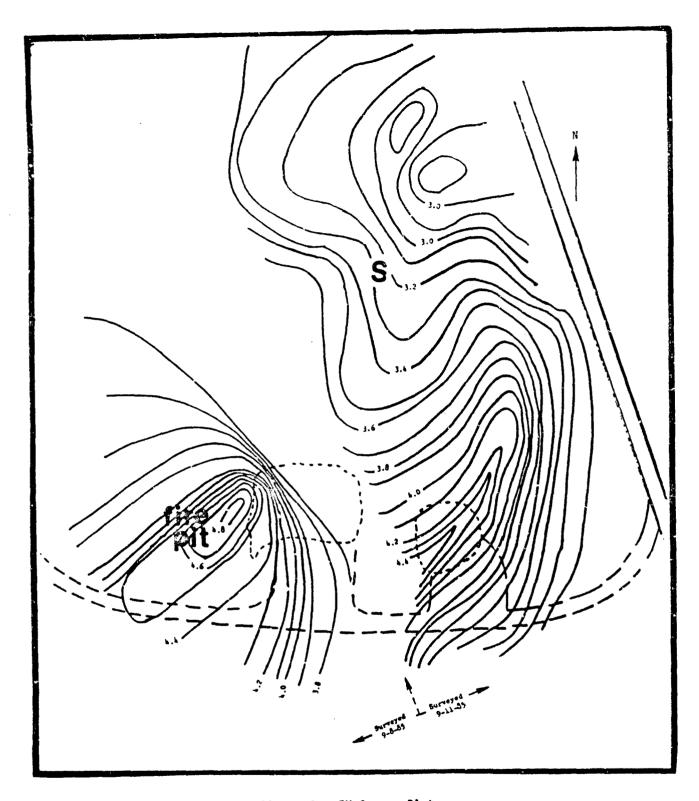
Soil Consolidation and headspace Vapors as a Function of Depth Figure 8.

D. ELECTROMAGNETIC SURVEY OF THE FIRE-PIT AREA

Recent work by the New Jersey Geological Survey, using electromagnetic methods, showed reasonable success in mapping a fire-training area plume. By using an induced electromagnetic field in soil or rock structure, it was possible to measure differences in the conductivity of the soil or rock and the solutions in the pore spaces. In the case of the work done in New Jersey, residual fuel, left over from fire training, had entered an unconfined sandy aquifer. Because of the similarities between these sites, it was decided to conduct an electromagnetic survey of the Volk Field site.

An electromagnetic survey was conducted around the pit area. Including all the land in the quadrant from monitoring well ET-1 north and west to the shallow well Q-17. The instrument used was an EM-34 manufactured by Geonic Ltd., Mississaugua Ontario, Canada. The EM-34 consists of a 2-foot (.61 meters) diameter coil of wire that transmits a burst of electromagnetic energy at a low frequency that induces electromagnetic excitation in conductive or semiconductive material. A second coil spaced at a prescribed distance from the transmitter receives the initial burst from the transmitter and the induced signal from the ground. These received signals are electronically transformed into a conductivity value for the "half space" between the coils. This technique is used to map rather large features of soil structure and not small things like metal drums. By moving the coils over an area of land in a grid pattern conductivities of half spaces can be plotted on a map. The coil spacing used on the survey that produced Figure 9 was 65 feet (20 meters). This results in a 100-foot (30 meters) depth of penetration of the induced signal.

Since organic contaminants seldom alter the conductivity of groundwater it was a surprise when measurable differences in conductivity in the aquifer mapped out in a potential plume pattern. A report on the New Jersey study (Reference 2) stated that the reason for the conductivity variation was that the fire-fighting foam "AFFF" acted as a conductive tracer for the fuel plume. We have concluded that the apparent plume at Volk Field was very likely the result of the extremely high soluble iron content, which coincides with areas of high organic contamination.



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Figure 9. EM Survey Plot.

Figure 9 is the resulting conductivity map near the pit. The initial eastern path of the plume is different than local groundwater motion to the northeast. Examination of the drilling logs reveals a less consolidated sandstone (less blows per foot) in that direction, affording the plume an easier route to the east. A turn to the north would be required to get the overall path of the plume on the general northeast course. A piece of data to help support the possibility of the plume reaching the point marked with an "S" in the figure is analytical data on soil taken in the root zone of an dying tree. The sample was taken from a depth of 12 feet (3.7 meters) using a 2-inch (5 cm) diameter hand auger. The analysis shows an oil and grease content in the 100 mg/kg range. An infrared trace indicating slightly oxidized oil (like the oil and grease found in the well field) also indicates the contaminated plume has reached this point.

SECTION III

SOIL WASHING

A. LABORATORY COLUMN EXPERIMENTS

Following initial site characterization, soil composites representative of contamination from the surface to 5 feet (1.7 meters) were taken from an area of high contamination and an area of lower contamination and transported to the laboratory for bench-scale column studies. Two, 3-foot (! meters) columns, 3 inches in diameter were packed to simulate the Volk Field soil profiles in areas of high and lower concentration. Table 2 provides details on the column and soils.

TABLE 2. CHARACTERISTICS OF SOIL COLUMNS

Column	Wet wt	Dry wt	Pore Vol	Porosity	ASTM Moisture	Packing Density	Column Height
#	(g)	<u>(g)</u>	(m1)	(%)	(%)	(g·cm ⁻³)	(cm)
1	7,980	7,830	1,230	27.5	1.88	1.97	98.6
2	7,985	7,880	1,160	26.3	1.35	2.02	97.3

Twelve pore volumes of 1.5 percent surfactant, consisting of a 50/50 mix of an ethoxylated alkyl phenol and ethoxylated fatty acid were passed through each column. Leachates from each pore volume wash were collected for analysis. An additional water rinse was passed through Column 1, only. After soil washing was complete, the columns were sacrificed and the top, middle, and bottom soils of each column were homogenized, extracted, fractionated, and analyzed with a Flame Ionization Detector-gas chromatograph (FID-GC).

Tables 3 and 4 show the fate of hydrocarbon pollutants with regard to the aliphatic, aromatic and unresolved constituents for the top, middle, bottom, and total column. Pretreatment values vary due to the nonhomogeneous (stratified according to sampling depth) method in which the columns were packed.

The data presented in Table 3 for Column 1 show an initial, pretreatment, total column contaminant level of 400 mg/kg aliphatic, 75 mg/kg aromatic and 1,003 mg/kg unresolved hydrocarbons. After treatment, these levels have been

reduced to 16.8 mg/kg aliphatic, 8.2 mg/kg aromatic, and 64.1 mg/kg of unresolved hydrocarbons. This relates to a 94 percent overall hydrocarbon reduction.

TABLE 3. FATE OF HYDROCARBON CONTAMINANTS -- SOIL COLUMN 1

Soil Hydrocarbon Content (mg/kg)

	Ali	Aliphatic		matic	Unresolved		
	Pretreat	Posttreat	Pretreat	Posttreat	<u>Pretreat</u>	Posttreat	
Тор	100	1.2	28.0	1.6	405	16.3	
Middle	140	4.5	25.0	1.6	320	7.5	
Bottom	160	11.1	22.0	5.1	278	40.3	
Total Colum	n 400	16.8	75.0	8.2	1003	64.1	

Results from Column 2 are presented in Table 4. As shown, the pretreated total column contaminant levels for aliphatic, aromatic, and unresolved hydrocarbons were 2.4 mg/kg, 3.42 mg/kg, and 16.7 mg/kg, respectively. Following treatment by surfactant washing, the hydrocarbon levels were reduced to .56 mg/kg of aliphatic, .07 mg/kg of aromatic, and 1.4 mg/kg of unresolved hydrocarbons in the entire column.

1ABLE 4. FATE OF HYDROCARBON CONTAMINANTS--SOIL COLUMN 2

Soil Hydrocarbon Content (mg/kg)

	Aliphatic <u>Pretreat Posttreat</u>		Aromatic <u>Pretreat Posttreat</u>		Unresolved <u>Pretreat Posttreat</u>	
Тор	1.4	.3	.3	.03	5.8	.9
Middle	. 7	.2	.1	.02	5.6	.9
Bottom	. 3	.06	.03	.02	5.3	nda
Total Column	1 2.4	. 56	.42	.07	16.7	1.4

A comparison of Columns 1 and 2 data shows that at the lower levels of contamination found in Column 2, surfactant was ing was less effective than in the higher levels of Column 1. This is to be expected because Column 1

contains a greater mass of unbound hydrocarbons. Another observation is that the percentage of hydrocarbon removal was greatest in the upper soil profile and decreased with depth. For instance, with regard to aliphatic hydrocarbon levels, the top portion of Column 2 was more contaminated, with 1.4 mg/kg than the middle section, with .7 mg/kg, which was more contaminated than the bottom section, containing only .3 mg/kg.

The effect of this contaminant profile was seen most dramatically in the aromatic fraction where the bottom portion of the column retains 85 percent of the original level. As the more contaminated top portion of the column was cleaned, the hydrocarbons were introduced to the less contaminated middle and bottom sections of the column where repartitioning back onto the soil can (and does) occur. This is not to say that effective cleanup has not occurred, since the mass of contaminants in the entire column decreased by more than 75 percent (from Table 4, Total Column Values). In summary, Column 1 experienced a 94 percent reduction in hydrocarbons while the less contaminated Column 2 produced a 75 percent removal. No significant decreases in column permeability were noted in the laboratory effort.

B. DETERMINATION OF INITIAL FIELD SOIL CONTAMINATION

To determine the concentration of nonvolatile contamination, oil and grease (0&G) tests were run on 36 soil samples taken at various depths and locations over the area of the pit. The oil and grease test requires the soil sample to be air-dried for 24 to 36 hours prior to extraction with carbon tetrachloride (CCl_4). Volatiles in the soil are not contributing to the mass of extract obtained.

The quantity of oil and grease extracted was measured in two ways. The first measurement used infrared absorbance at a wave number of 2910 cm-1 (equivalent to a wavelength of 3.436 microns). Because the O&G values were so high for most of the samples, it was possible to evaporate off the carbontetrachloride on a steam bath and weigh the organic residue in a beaker. Agreement between these two methods was quite good. As expected, the concentrations determined after evaporation from the steam bath were slightly less than those calculated from the infrared method. Figure 6 showed the overall distribution of CCI₄ extractable oil and grease as a function of depth. Oil and grease values were highest near the fire pit surface, decreased with depth, and then increased in soil slightly below the water table. A gas chromatograph analysis was conducted to measure the relative

quantities of aliphatics, aromatics, and "unresolved" compounds extracted from the soil. (See Table 5). This analysis does not account for many of the heavier, more complex hydrocarbons and produced a total hydrocarbon concentration an order of magnitude lower than the O&G measurements at the same depth.

TABLE 5. HYDROCARBON CHARACTERIZATION OF VOLK AFB SOILS

Resolved Compounds (ug/g)

Sample/Depth	Aliphatic <u>Fraction</u>	Aromatic <u>Fraction</u>	Polar <u>Fraction</u>	Unresolved Total (ug/g)
Pit 1/Surface (1)	132	36.2	8.75	1,160
Pit 1/Surface (2)	341	42.1	58.6	1,590
Pit 1/1.5 feet	138	33.3	8.29	498
Pit 1/3 feet	218	82.4	14.5	206
Pit 1/5 feet	622	77.4	1.59	458
Pit 2/Surface	71.4	66.2	3.97	254
Pit 2/2.5 feet (1)	65.0	14.0	.564	87.0
Pit 2/2.5 feet (2)	8.33	8.31	.485	15.8

It was important that the fire-training area soil to receive in situ treatment remain undisturbed. The wash fluid's path could not be influenced by sampling methods that created preferential hydraulic paths. Six samples were taken next to the test cells to establish prewash levels. The measured O&G values appear in Table 6. These values vary as much as -73 percent and +50 percent from the average. Since coefficients of variation for replicate O&G measurements average 12 percent, this variability for prewash levels was a major drawback in analyzing the significance of postwash data.

TABLE 6. PREWASH OIL AND GREASE MEASUREMENTS

Sample No.	4055	4056	4057	4058	4059	4060
O&G mg/kg	5400	1850	5800	5050	1050	4060

The total amount of extractable material in the 4,000 yd³ (3,200 m³) study area can be approximated by segmenting the scil column below the pit into 10 equal thicknesses. The average concentration of the 10 imaginary slabs of soil was then multiplied by the average weight of the soil. Using this approach and referring to Figure 6 for average concentrations, the total extractable hydrocarbons remaining in the vadose zone is approximately 1,500 gallons (5,700 liters).

C. TEST CELL LAYOUT

To determine the soil-washing ability of a number of surfactant solutions, a series of seven test areas were established in the fire pit. The locations of the areas were chosen to provide as near a uniform contamination level as could be predicted from oil and grease measurements. Because of the impenetrable heavy oil and soot accumulated at the pit surface, the top foot of the soil was removed from each test area. Three of the test areas measured 2 feet by 2 feet by 1 foot deep, and four of the areas were 1 foot by 1 foot by 1 foot. The 1-foot depth eliminated the carbonized oil layer and provided suitable initial percolation rates.

D. WASH SOLUTIONS

Two terms are used to describe the surfactants: "synthetic," and "natural." The synthetic surfactants are those that have been manmade by chemical processes and are available commercially. The natural surfactants are fatty acid and ester compounds that are by-products of biological breakdown of fuels and oils beneath the pit. (Reference 3) Although the concentration of these natural surfactants averaged only 250 mg/l in the groundwater, the use of these surfactants to clean the soils was an interesting possibility. Both untreated groundwater with surfactants and treated clarifier effluent were used as was solutions. The synthetic surfactants used for the pilot treatment study were:

- 1. Surfactant 1 (S1). A mixture of ethoxylated fatty acids sold by Wilco Chemical Corporation (used in agriculture as a soil penetrant).
 - 2. Surfactant 2 (S2). An ethoxylated alkyl phenol (Diamond Shamrock).
- 3. Surfactant 3 (S3). An anionic sulfonated alkyl ester (Diamond Shamrock.

E. WASHING PROCEDURES

The rate of addition of wash solution was set at 3 inches per day (76 mm) based on expected percolation rates. This corresponds to 1.87 gallons (7.1 liters) per day for the smaller test areas and 7.48 gallons (28.3 liters) per day for the larger test areas. Wash solution was added four times a day for 4 or 6 consecutive days depending on the availability of the surfactant solution. An unexpected decrease in percolation was observed in most of the test areas. The 14-pore volume target was reached in only three test cells and, eventually, two of the test holes plugged completely. Table 7 summarizes the types and quantities of each surfactant applied to the test areas.

gallons (7 or 282) of clean, upgradient well water. Before the rinse period was finished and before soil samples could be taken, 4 inches (10 cm) of rain fell over a 3-day period. Attempts to keep the test beds from filling up with runoff by using berms at the surface were ineffective. The rinse phase of the pilot study was unexpectedly extensive. The mobility of contamination from other areas of the pit to the test bed is unknown. An 0.25-inch (6.3 mm) layer of fine, dark silt was observed at the bottom of each test bed following the rain. It was sharply defined by texture and was easily separated from the original soils.

TABLE 7. WASH SOLUTION VOLUMES AND CONCENTRATIONS

	Wash	Surfactant	Total	Pore	
Area #	# Solution	Concentration	Vol. (gal)	Volumes	
ì	Natural surfactant +S3	0.025%	22 plugged	7	
2	Natural surfactant	0.024%	32	10	
3	Natural surfactant	0.024%	29	9	
4*	Clarifier effluent	0.015%	7	9	
5*	Clarifier effluent	0.015%	7	9	
6*	S3	0.5%	11	14	
7*	50/50 \$1/\$2	1.5%	11	14	

^{*1} ft² cross section holes

E. SAMPLING AND ANALYSIS

After washing and rinsing the soil below each of the test beds, samples were taken from: the surface of fine material at the bottom of each bed, soil from 2-4 inches (50-100 mm) and soil 12-14 inches (300-360 mm) from the bottom of the bed. The samples were placed in wide mouth glass jars. The jars were then placed in cartons for transportation to the analytical lab at the EPA's Oil and Hazardous Materials Simulated Environmental Test Tank (OHMSEII) in Leonardo, New Zersey. At OHMSEIT, the soil samples from each test bed were extracted (and analyzed using an infrared spectrophotometer) to determine the remaining oil and grease. In Figure 10, two bar charts are presented to aid in the understanding of the postwash data. Each bar represents the O&G residual remaining in a specific surfactant test bed, as labeled on the horizontal axis. The dashed lines across each bar chart represent the range of prewash O&G values. Although a larger number of samples were needed to statistically quantify these results, the surfactant solutions did not significantly reduce O&G from prewash concentrations.

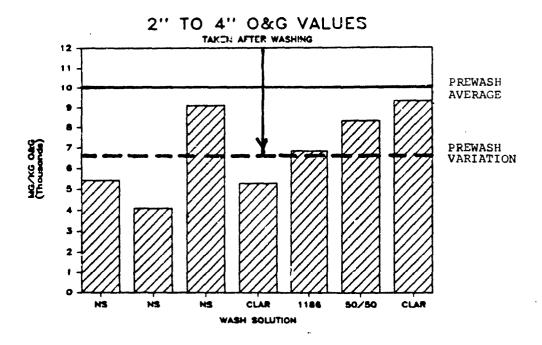
F. CONCLUSIONS OF IN SITU SOIL WASHING AT THE VOLK FIELD FIRE-TRAINING PII In spite of the repeated successes of the engineered surfactant to clean contaminated soils in laboratory tests, there is little evidence that the soil was cleaned in situ at Volk Field. Within statistical limits, there is no significant difference in pre- and postwash soil contaminant levels.

As stated previously, laboratory columns were packed with Volk Field soil washed with 12 pore volumes of the 50/50 mix of engineered surfactant and rinsed. At 1.5 percent, the solution was effective in removing 75-94 percent of the hydrocarbons from samples of fire pit soil. In this work, 14 pore volumes passed through the test soil with no measureable effect. This initial field test of <u>in situ</u> soils washing has raised serious doubts over its full-scale feasibility.

Although the laboratory columns were packed to simulate <u>in situ</u> conditions, the noticeable reduction in soil permeability was not predicted in the laboratory. This underscorer the importance of small pilot-scale testing on all contaminated sites before to full-scale design of decontamination technologies.

A major concern of <u>in situ</u> soils washing which must addressed before renewed laboratory testing is the need for a biodegradable surfactant which will not reduce soil permeability. The surfactant must not persist in the

groundwater and continue to mobilize contaminants after pumping is stopped. Additional research is also needed on methods of recovering and reusing surfactants for multiple passes through the soil. To accomplish this, a treatment system must be devised to separate organic contaminants from surfactant rinse waters.



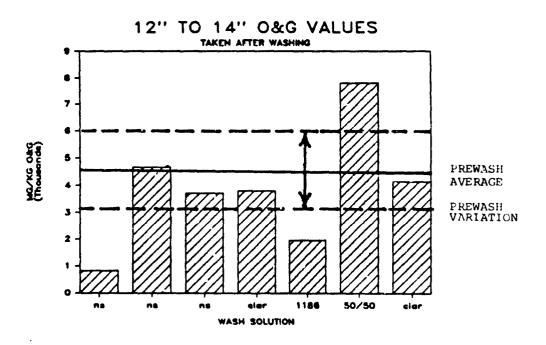


Figure 10. Pre- and Postwash Oil and Grease Data

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SECTION IV

GROUNDWATER CONTROL AND TREATMENT

A. REQUIREMENT FOR GROUNDWATER TREATMENT

The original plan for this demonstration in situ soils washing required a network of withdrawal wells to produce a wash solution and create a capture zone for the surfactants and released contaminants. Because of the high level of contamination in the groundwater below the fire pit, the treatment pilot study was expanded to include a groundwater pretreatment system. The poor condition of the groundwater is indicated by TOC measurements averaging over 200 parts-per-million across the well field. Biochemical oxygen demand averaged 50 mg/L. Soluble iron levels exceeding 20 mg/L were measured in one well, while upgradient wells measured only .3 mg/L. The pH was 5.5 to 6.0 and required 60 to 180 ppm lime to bring the pH to 7.5.

The groundwater contaminants of greatest concern were benzene, toluene, ethyl benzene and xylenes which are all volatile components of JP-4 jet fuel. Total volatile aromatic hydrocarbons were present at concentrations of 10-20 mg/liter. Although the pilot study was not equipped for extensive GC/MS analysis, trace levels of trichloroethylene and 1,1,1 trichloroethane were also detected.

B. WELL FIFLD SPECIFICATION & PERFORMANCE

The new well field consisted of six production wells, in addition to seven monitoring wells that had been installed 4 months earlier. Figure 11 shows the location of each well and Appendix B contains well boring logs. The wells were drilled using a 5 7/8-inch auger and wash method and cased with 4-inch Schedule 40 threaded PVC. Screens were also Schedule 40 PVC with a slot size of 0.010 inch. Backfill around the screen was Number 30 flint sand.

Each production well had a stainless steel submersible pump with a low-water, shutoff monitor. A throttle valve was installed at each well head. The wells were connected to a common pipe to carry the contaminated water to either the chemical/physical treatment system or the equalization pond. To prevent water from entering a well if it was not pumping, check valves were installed at each well head.

During the drilling operation, split-spoon soil samples were taken at

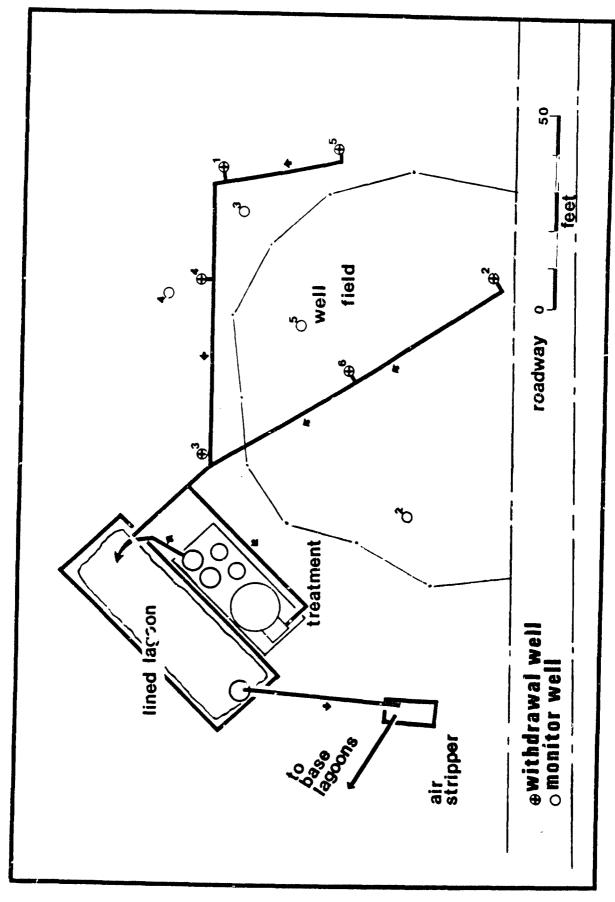


Figure 11. Well Field Layout

5 foot intervals. At the same time, penetration tests were run to determine the degree of consolidation of the soil. Using a 140-pound weight, the split-spoon sampler is driven into the soil through the end of the hollow-stem auger. The number of blows required to drive the sampler 1 foot is reported in Appendix B. From the resulting penetration values and the drill operator's observations, it was apparent that sandstone is encountered at 11 to 14 feet below the surface. Figure 12 shows the equipotential lines of the water table near the pit.

The first pumping test was attempted using the production well WW-1. The yield of that well was so low, because of contamination, that the test was postponed until WW-2 was ready. Since the purpose of the first pumping test was to evaluate only the aquifer directly below the pit, only 8 hours of pumping were necessary. The rate of pumping was 12 gpm/min. Drawdown was measured in the production well itself and in monitoring wells ET-2, ET-3, and ET-5. Table 8 summarizes the drawdown and recovery data.

The elevation of groundwater in each of the wells is reported in Table 8 in feet from mean sea level at the time specified to the left of each row. The top row of numbers reports the elevation of each of the well heads. The data from ET-2 and ET-5 was taken electronically, using pressure transmitters; the remaining elevations were calculated from measurements using a resistance probe on a premeasured wire to detect the water surface. Based upon drawdown data from wells ET-2, ET-3 and ET-5, and using the Theim Equation, the transmissibility of this shallow aquifer is estimated at 1,800 gallons per day, per foot. This figure agrees with literature values for shallow, fine-sand formations.

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The second pumping test was done to evaluate the effect of ali six production wells operating at once. Using the ball valve at each of the well heads, individual wells were throttled to maintain a constant flow without initiating low water-level cutoffs. The maximum sustained production from all six wells was only 29 gpm. WW-2 was turned off at the end of the test and the five remaining wells produced 20 gpm. The total production of WW-1, WW-3, and WW-5 was only 3-5 gpm, due primarily to the heavy organic contamination and iron precipitation near the well screens.

During the initial pilot study, the well field was pumped for 12 days and approximately 11 hours per day. During one day, 3 inches of rain fell on the site. Water-level sensors detected this precipitation 20 to 35 hours later.

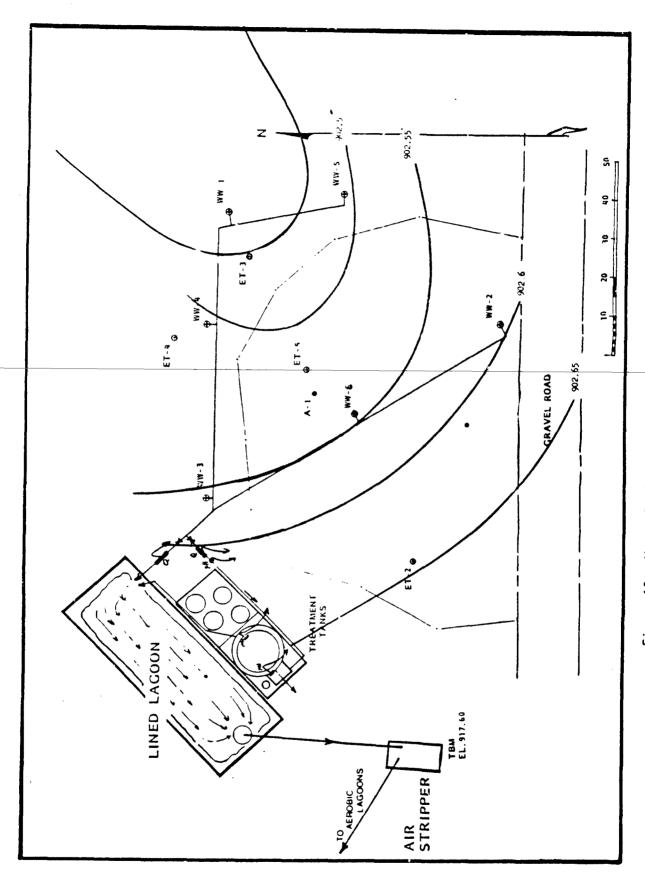


Figure 12. Water Equipotential Lines Before Pumping

TABLE 8. PUMP TESTING OF PRODUCTION WELL WW-2

Time (min)	WW-2	J-10	E T- 2	ET-5	ET-3	WW-1
0 0.5 1 1.5 2 2.5 3 3.5	919.09 902.59 896.19 895.59 895.09 894.79 894.79 894.79	919.36 902.61	919.33 902.63	918.75 902.55	917.46 902.46	917.92 903.32
4 5 6.5	894.69 894.59	902.56			902.46	903.32
7.5 10	894.49	902.56			902.46	903.32
15 16 24	894.39 894.29		902.578	901.977	902.46	
29 45 60 75	894.09	902.56 902.46 902.41 902.36	902.546 902.536 902.536	901.94 901.932 901.943	000.76	002 20
120 150 180	894.09		902.51 902.502 902.492	901.914 901.907 901.897	902.36	903.32 903.32
240 300 360 480 495 510 540 660 720 780 840 960 1020 1200		200.56	902.479 902.464 902.463 902.473 902.477 902.485 902.525 902.546 902.563 902.577 902.589 902.601	901.882 901.854 901.854 901.875 901.895 901.902 901.915 901.925 901.925 901.985 901.997 920.011 902.021	902.36 902.26 902.26	903.32 903.32 903.32 903.32
1320	902.59	902.56	902.629	902.047	902.46	903.32

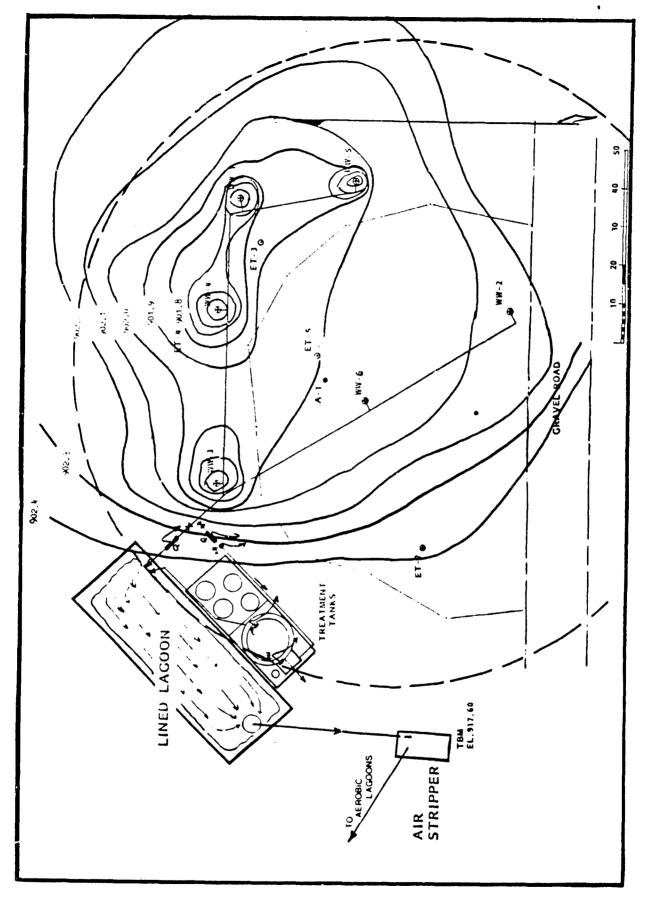


Figure 13. Equipotential Lines During Pumping

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indicating an unsaturated vertical permeability range of 5 X 10⁻³ to 1 X 10⁻⁴ cm/sec and that an artificial recharge rate of 2 to 3 inches per day was possible under optimum conditions. The total amount of fluid pumped from the ground during the pilot study was approximately 85,000 gallons. Subsequent pumping under HQ AFESC/RDVW supervision has brought the total to 465,000 gallons. Equipotential lines during pumping are shown in Figure 13.

C. GROUNDWATER TREATMENT SYSTEM

Although the primary objective of this research was a soils washing demonstration, the highly contaminated groundwater also provided a major research challenge. To use the contaminated groundwater for the soil washing solvent, it was first necessary to remove high levels of hydrocarbon contamination.

Total organic carbon (TOC) measurements were by far the most numerous and precise of all the analyses run on the groundwater. With coefficients of variations between 1 and 5 percent, TOC values provided an accurate assessment of hydrocarbon contamination in the groundwater and removal in the treatment system. EPA Method 624 was used to define the volatile fraction of the total hydrocarbons and provide general information on volatile removal rates.

The initial concept for groundwater treatment was to pump water to an equalization pond then treat it using a packed-tower air stripper. However, when extensive precipitation of iron-organic floc was observed during site characterization, a method of chemical pretreatment was developed. Groundwater was subjected to a number of jar tests to determine the optimum chemical additions. Additives tested included: lime, sulfuric acid, hydrogen peroxide, alum, ferric chloride, polymers and emulsion breakers. A lime addition to raise the pH from 6.0 to 7.0-7.5, produced the optimum oxidation and precipitation of the ferric hydoxide-organic complex. A flash mixer and 4,500 gallon clarifier were placed between the equilization pond and air stripper to remove these solids.

A flow diagram from the aquifer to the effluent end of the air stripper is shown in Figure 14. The sampling points along the flow path are numbered and correspond with sampling data found in Table 9. Four sets of data are presented in Figure 15 to illustrate TOC reduction through the system. These bar charts show the well field effluent, the clarifier effluent, the air-stripper feed and finally the air-stripper effluent to the sewer. The second bar in each set is the clarifier effluent. The apparent

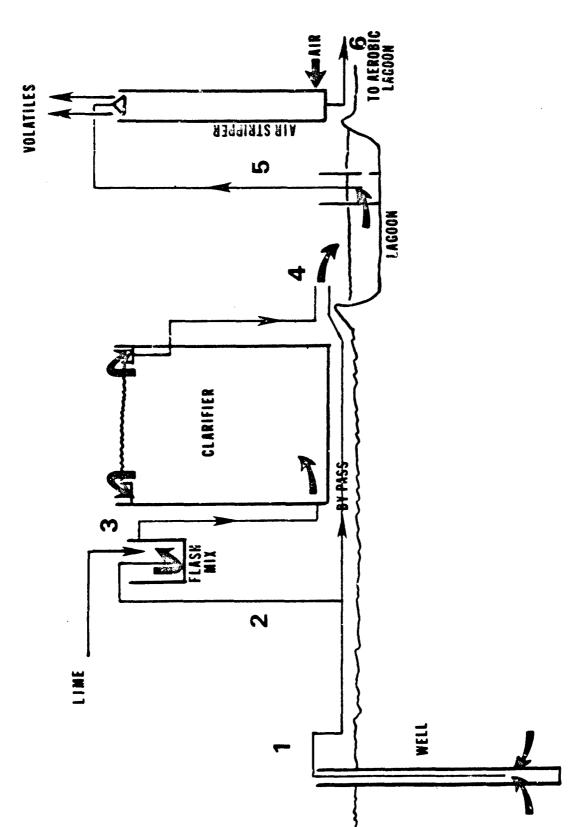


Figure 14. Volk Field Pilot Treatment for Water

TABLE 9. GROUNDWATER TREATMENT RESULTS

Pt No.	Description	Tests Performed	Average Or Range Of Values
1	Individual wellheads	volatile organic total organic chemical oxygen demand oil and grease pH	10-20 mg/liter 60-760 mg/liter 6-500 mg/liter 0.2-46 mg/liter 5.1-6.2
2	Combined well field	volatile organic total organic iron pH fiow rate	10-20 mg/liter 250 <u>+</u> 14% mg/liter 32 mg/liter 6.0 <u>+</u> 0.2 24-28 gpm
3	Flash mixer effluent	total organic (dissolved) suspended solids pH flow rate	160 mg/liter 350 mg/liter 6.8-9.7 9-28 gpm
4	Clarifier effluent	total organic suspended solids pH flow rate	155 mg/liter 13.6-104 mg/liter 7.6 9-28 gpm
5	Air-stripper feed	volatile organic total organic temperature flow rate (water) cil and grease	3.5-7.0 mg/liter 151 <u>+</u> 13% mg/liter 6-15 ⁰ C 15-20 gpm 3.6 mg/liter
6	Air-stripper effluent	volatile organic total organic flow rate (air) oil and grease biochemical oxygen demand chemical oxygen demand	0.5-0.3 mg/liter 146 mg/liter 215 cu.ft/min 3.6 mg/liter 25 mg/liter 180 mg/liter
7	Clarifier	suspended solids	4.4 mg/liter
8	Clarifier bottom	suspended solids	2331 mg/liter
9	Soil	oil and grease	800-16000 mg/kg

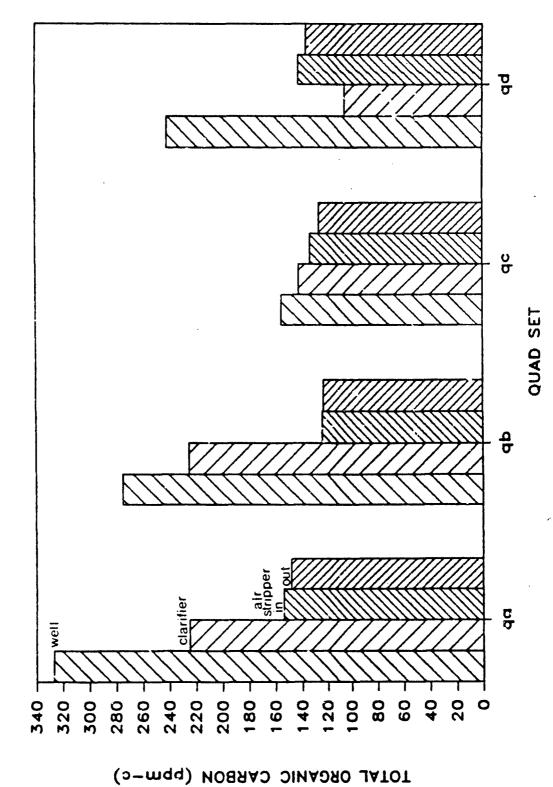


Figure 15. TOC Reduction in Water Treatment Process

increase in TOC in set "qd" could be attributed to the unmixed condition of the 16,000 gallon lagoon or a sampling error. The small reduction in TOC through the air stripper confirms that volatiles make up only 3-4 percent of the total TOC in this aged oil and fuel contamination.

Water from the flash mixer entered into the bottom of the clarifier which provided a 3- to 4-hour settling time and resulted in a 98 percent reduction in suspended solids. Effluent from the clarifier then entered the 16,000-gallon lined aeration pond. This additional aeration further created more iron oxidation and precipitation. The pond's large surface area and average retention time of 48 hours were extremely useful for removing volatiles. An analysis of all volatile compounds detected using EPA Method 624 showed that 60 percent of the volatiles were removed in this stage. Equalization ponds should be considered for any groundwater treatment where the space is available and air emissions do not pose a regulatory problem. In addition to their treatment potential, they provide flexibility and promote a more continuous operation.

Removal of remaining volatile organics was accomplished in a packed tower air stripper provided by the HQ AFESC Environics Division. The tower contained an 8-foot high, 1.5-foot diameter column of 3/8-inch Pall-Rings, and was designed to treat 50 gpm at an air-to-water ratio of 40:1. Because of a reduced groundwater production, the flow rate through the air stripper averaged 28 gpm creating an air-to-water ratio of approximately 80:1. This improved overall performance, particularly for less volative xylenes and toluene. The air stripper effectively removed an average of 96 percent of the BTX entering the stripper and reduced all chlorinated hydrocarbons to less than 5 ppb. The 15 pounds-per-day total volatile emission standard was not approached as the maximum emissions from both the pond and tower was only 4 pounds per day.

The Wisconsin Department of Natural Resources approved a temporary discharge of air-stripper effluent to the Volk Field wastewater treatment system. An average of 11,000 gpd of treated groundwater was conveyed to two onbase facultative wastewater lagoons. Numerous laboratory and field studies have confirmed that fuel hydrocarbons are rapidly degraded in aerobic wastewaters (Reference 4). Although it could not be proven due to the extreme dilution factor, it can be assumed that remaining fuel hydrocarbons were extensively degraded during the 180-day retention time in these lagoons.

SECTION V CONCLUSIONS AND RECOMMENDATIONS

A. GENERAL SITE CONDITION

The extensive field study conducted at the Volk Field fire training area has revealed a number of interesting site conditions and potential decontamination processes. As site characterization proceeded, several of our initial assumptions and test procedures had to be modified as new observations were made.

One of the most important observations was the absence of a floating layer of petroleum, despite the estimated 50,000 gailons of fuel and oil that had soaked thru the soil. What was found was a concentrated mixture of emulsified fuels and oils which extended at least 10 feet below the groundwater soil interface. This extensive emulsification was the result of two surfactant interactions. The large amounts of firefighting foams used at the site provided a synthetic surfactant source, while the biological breakdown of fuels and oils produced fatty acids and esthers which also acted as natural surfactants. The depth and emulsified nature of the contamination required a much more extensive groundwater treatment system than was anticipated. The soils beneath the Volk Field fire-training pit remain contaminated with oils and fuel residues. Approximately 4000 cubic yards of soil were contaminated with 12,000 to 15,000 pounds of hydrocarbons.

B. SOILS WASHING

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- 1. Despite the repeated success of engineered surfactants to clean contaminated soils in laboratory column tests, no data was obtained in the Volk Field test to statistically confirm that in situ soils washing is a viable method of soil decontamination. If soils washing did occur, it was much less effective than the 75-94 percent achieved in laboratory column tests.
- 2. Repeated washings of soils with several surfactant solutions actually led to a noticeable reduction in soil permeability. This clogging effect had two potential causes: surfactant micelle formation in the pore spaces, or a surfactant-enhanced movement of fine particles down the soil structure until they fill in the pore spaces deeper in the soil. Neither of these theories has been confirmed, and both represent areas needing additional laboratory research.
- 3. The cost of using synthetic surfactants for multiple washings of large volumes of contaminated soil is also very high. The estimated cost of the

surfactants for removing 25,000 gallons of oil and fuel at Volk Field would be \$540,000. The high cost stems from present inability to economically separate organic contaminants from the surfactant solution and reuse the surfactant.

4. Until these serious problems are overcome, <u>in situ</u> soils washing should not be advanced to full-scale development.

B. GROUNDWATER TREATMENT AND HYDRAULIC CONTROL

- 1. The groundwater treatment system described in Section IV removed 95-99 percent of the contaminants of concern: benzene, toluene, ethylbenzene, xylenes, trichloroethylene and trichloroethane.
- 2. The two standards set by the Wisconsin Dept. of Natural Resources were easily achieved. The average BOD₅ discharge per day of 12 pounds was well within the 60 pounds-per-day limitation. The release of 2-4 pounds of volatiles per day did not approach the 15-pound-per-day limit.
- 3. The total organic carbon content of the groundwater was reduced by an average of 40 percent, primarily through coprecipitation with iron hydroxides in the clarifier and pond.
- 4. High organic levels at the soil and groundwater interface have depleted available oxygen and created strong reducing conditions with a pH of 5-5 to 6.0. This reducing environment has caused iron within the sandstone to solubilize and form an iron "plume," which may have been detected during geophysical resistivity mapping. Dissolved iron levels as high as 24 parts per million were measured in the center of the organic plume.
- 5. Adjustment of the groundwater pH to 7.5 using lime addition and removal of the iron-organic floc in a clarifier was a necessary pretreatment to reduce clogging of the air stripper.
- 6. The total volume of contaminated water pumped from beneath the pit between September 7 and November 14, 1985 was 464,000 gallons (1,760,000 liters). This is more than twice the volume of water contained in the study volume. Analytical data shows the contamination levels from the well field were not significantly educed after 2 months of pumping. This could be partially explained by the 12-hour-on and 12-hour-off pumping schedule which allowed soil contaminants to equilibrate in the groundwater when the pumps were off.
- 7. The groundwater does not appear to be toxic to all biological life since Water Boatmen (Insect order <u>Hemiptera</u>, family <u>Corixidae</u>) were able to thrive in the equalization pond.

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APPENDIX A

ANALYTICAL METHODS AND QA/QC SUMMARY

APPENDIX A

ANALYTICAL METHODS AND DA/OC SUMMARY

The analyses were directed at common volatiles and the total nonvolatile organic compounds. Identification of specific compounds was limited to benzene, toluene, ethylbenzene, trichloroethylene, and 1,1,1 trichloroethane. Although other volatiles were detected, adequate standards were not available in the field lab to identify all peaks.

The methods of evaluation were:

- 1. Gas chromatography was used to determine the removal of volatile components (EPA Method 624).
- 2. Total organic carbon (TOC) was measured to determine treatment effects on all the organics.
- 3. Suspended solids was measured to determine the physical form of the contaminant.
 - 4. pH was measured as a control function.
- 5. Chemical oxygen demand (COD) was measured as an "u!timate" biological oxygen demand.
- 6. Biological oxygen demand (BOD) was measured to comply with the 60 pound/day BOD limit required by the State of Wisconsin.
- 7. Oil and grease (O&G) using carbon tetrachloride extraction was used as a gross indicator of residual jet fuel and oils remaining in the soil and groundwater.
- 8. Dissolved oxygen (DO) measurements were made on selected groundwater samples to determine the impact of hydrocarbon degradation on oxygen levels and the oxidation potential of iron in recovered water. The BOD $_5$ test also required an understanding of aquifer DO.
- 9. Drawdowns and pumping rates were measured to monitor the cone of influence and groundwater movement.

The quality assurance objectives set forth in the Quality Assurance Plan were difficult to achieve, given the wide variation in contaminant levels found at this site. Several QA objectives were not achieved. Of most concern were the results of the field lab's gas chromotagraph. Interlab data from the Environics Laboratory at Tyndall AFB showed the field measured data to have an average positive bias of 31 percent in the parts per million range. Collocated analyses in the hundreds of parts per billion range had a coefficient of variation of 150 to 210 percent. Performance Evaluation

Standards sent by the EPA-Edison labs were also measured with a high positive bias. Although this apparent high positive bias was unacceptable for measuring volatiles in the 1-100 parts per billion range, the field GC was still a valid indicator of total volatile removal rates in the 10-20 parts per million range occurring in the treatment system.

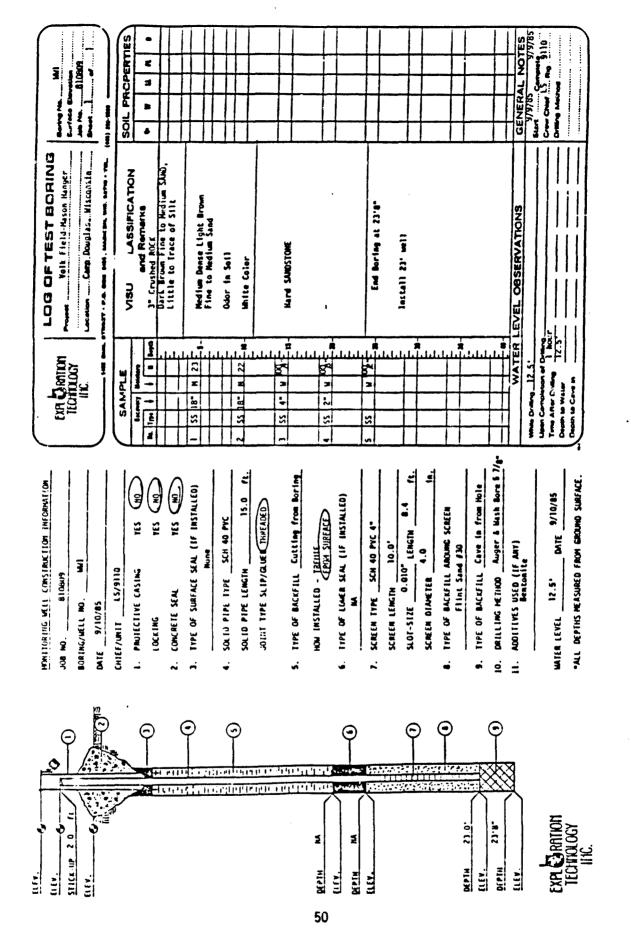
Biochemical oxygen demand measurements showed a negative bias of 9 percent compared to collocated samples run at Tyndali AFB. The plan called for \pm 5 percent. Chemical oxygen demand \pm 5 percent in the plan had a coefficient of variation of 35 percent. Oil and grease was to be \pm 5 percent and turned out to be 12 percent CY on replicate runs and 6 percent CV when two methods were compared. The strongest data was from TOC analyses. Replicate samples had a CV of 2 percent, collocated, a CV of 12 percent. Table A-1 is a summary of this QA data.

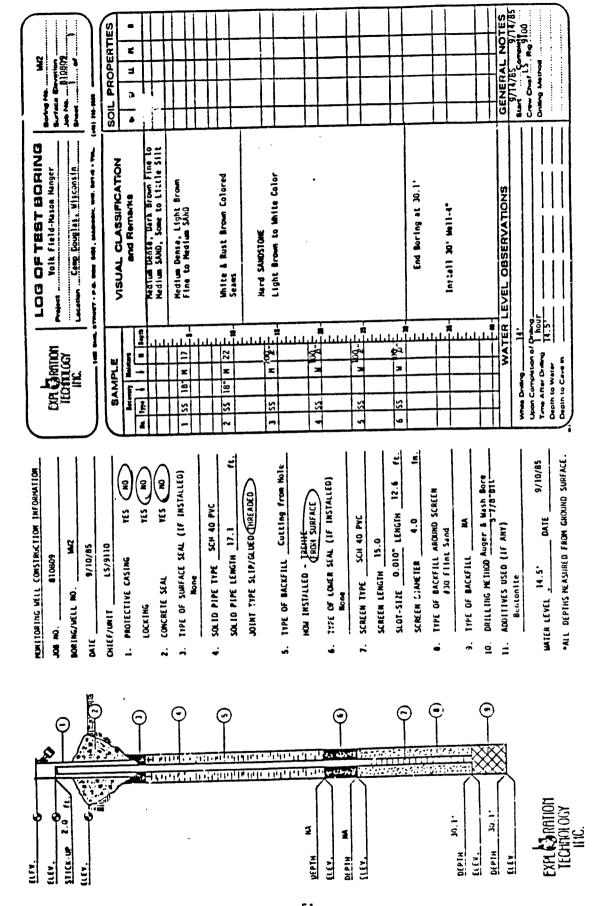
TABLE A-1. QA REPORT TABLE

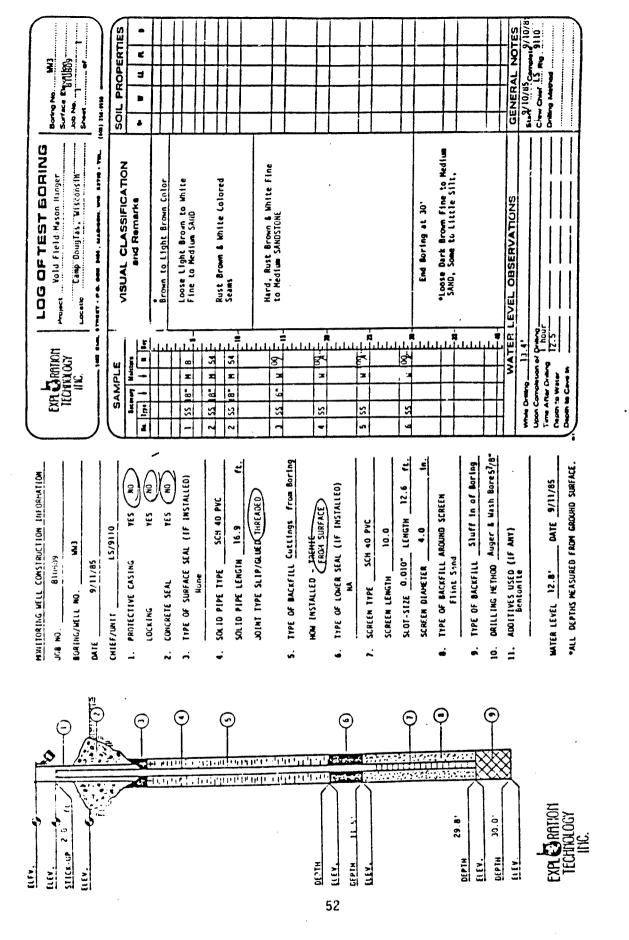
Grands Performance Evaluation Well Field Effluent Fetention times Fetention Tolucne Ethylbenzene Air Stripper Feed Enzene Tolucne Ethylbenzene Tolucne Ethylbenzene Tolucne Ethylbenzene Tolucne Tolucne	(K) (K) (K) (K) (K) (K)	76. of 168ts 3	Ave (ppm)	2 5	Mo. of Samples	(rdd)	<u>ن</u>	No. of Samples	Į.	Sample
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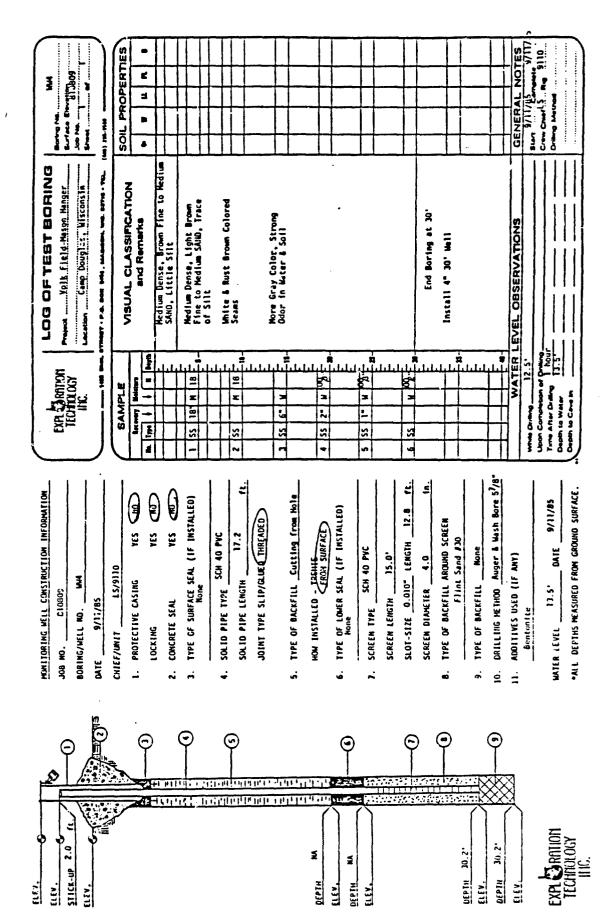
APPENDIX B

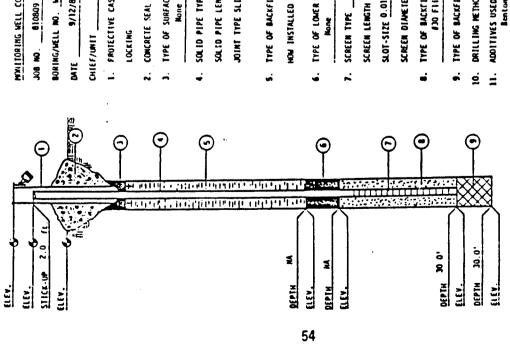
WITHDRAWAL WELL BORING AND WELL LOGS





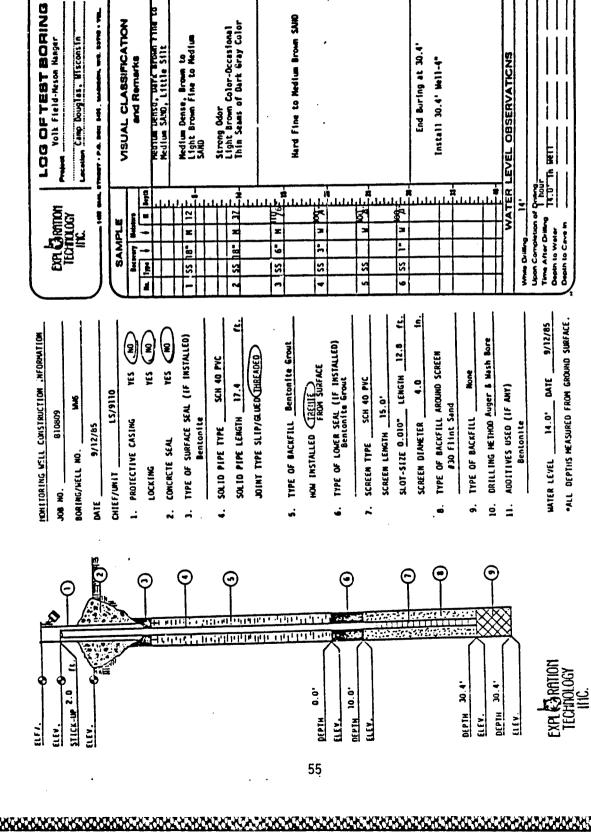






MYNITORING WELL CONSTRUCTION INFORMATION	N INFORMATION					Ì	
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			Preject VOIR FIELD-Mason Hanger			İ	i
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		7 7 7 7 7	Brown to White Color		H	$oxed{\sqcup}$	\coprod
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SLOT-SIZE 0.010" LENGTH	12.8 €.	- 1 SS 9	•	1	+	\dashv	_
SCREEN DIAMETER 4.0	ta.		End Boring at 30'		+	+	\perp
8. TYPE OF BACKFILL AROUND SCREEN	SCREEN	 					
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			SAND, Occasional Seams of	$\frac{1}{1}$	╀	4	
9. ITPE OF BACKFILL MONE		لىك	Dark Brown Color Norbled				
10. DRILLING METHOD Auger & Wash Bore	Wash Bore		1120 21111 21	1	+	4	1
11. ADDITIVES USED (IF ANY)					+	\downarrow	
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13.2' 13.2'	9/12/85	The Annual Constitution of Orlean		Concounts. mg 9110	á	I	2
MIER LEVEL DATE		Depth to Water 13.2		Orthog Mades	ļ	•	
*ALL DEPTHS HEASURED FROM GROUND SURFACE.	NOUND SURFACE.	•					

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SOIL PROPERTIES

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GENERAL NOTES Sen 9/12/85 mm 9/12/8 Cru Out 15 mg 9/100